Electronic Supporting Information

Cross Structured Two-dimensional Violet Phosphorene with Extremely High Deformation Resistance

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1. Preparation of substrate
The silicon substrate, coated with 300 nm SiO\textsubscript{2} patterned by 1 \textmu m and 1.5 \textmu m diameter holes with depth of about 500 nm produced by Suzhou in-Situ Chips Technology Ltd. The substrate was immersed in acetone, alcohol, and distilled water subsequently by ultrasonication for 10 minutes to remove the impurities. The residual liquid on the surface was then removed by a nitrogen gun.

2. Preparation of suspended violet phosphorene nanoflakes
Violet phosphorene nanoflakes were prepared by a mechanical exfoliation method. The area of the tape with the sample was stuck to the area of the silicon wafer with the holes. The tape was keeping at a constant temperature of 80 °C for 30 min and then removed.

3. Force curve measurements
Atomic force microscope (AFM) system (Dimension Icon, Bruker) was used to obtain the force curves by a PF-QNM mode. The probe model is RTESPA 525. The parameter is 8 nm (tip radius), 125 \textmu m (length), 10-15 \textmu m (tip heigh) and 40 \textmu m
4. TEM characterization

![TEM Image](image)

Fig. S1 TEM image of violet phosphorene (inset shows the cross structure).

5. Raman and XRD features of violet phosphorene nanoflakes

![Raman and XRD Graphs](image)

Fig. S2 (a) Raman (633 nm), (b) XRD characterization of violet phosphorene nanoflakes.

6. Characterization of AFM tips

The SEM image of tips before and after a single-point force curve test have been measurements (Fig. S3a and b). The damage of the probe is negligible by a single-point force curve test. No obvious damage has been observed from the probe after single-point repeat force curve measurements (Fig. 2e, article). These analysis results ensure the accuracy of the experimental results. The probe is in contact with the sample or substrate during measurements. The AFM tip has been damaged after long-term measurements (Fig. S3c).
Fig. S3 (a) before and (b) after single-point force curve test. (c) after long time measurements.

7. Calibration method of AFM cantilever

The force curve test is used to analyze the mechanical properties of the nanoflakes. The deflection sensitivity was corrected before a force curve test. This value is required by the system to convert the spot offset voltage signal detected by the photodetector into the actual bending of the cantilever in order to study the mechanical properties of sample. Two steps were required for the deflection sensitivity measurements. The force curve on the hard sample (sapphire) was first obtained. The displacement zone when the probe is gradually approaching to contact with the sample from the force curve was then selected to calculate the deflection sensitivity. The force applied to the sample was obtained by the bending of the probe cantilever and the elastic coefficient \( k_c \) of the probe through Hook's law \( F = -kx \). The elastic coefficient \( k_c \) (rectangular cantilever) was obtained by the Sader method. The equation is:

\[
    k_c = 7.5246 \rho_f \omega^2 L Q f_0^2 \Gamma_1(Re) \quad Re = \frac{2\pi \rho_f f_0 \omega^2}{4n_f}
\]

where \( L \) is length, \( \omega \) is width, \( f_0 \) is resonance frequency and \( Q \) is quality factor of the cantilever beam.

8. First-principles calculation of violet phosphorene nanosheets Poisson's ratio

All our calculations were performed using the plane-wave Vienna Ab initio Simulation Package (VASP). A projector augmented-wave (PAW) pseudopotential method was applied to describe interactions between core and valence electrons. A kinetic energy cutoff of 500 eV and the first Brillouin zone sampled with \( 3 \times 3 \times 1 \) k-point grid were adopted. These parameters are necessary for convergence of the total energy to within \( 10^{-7} \) eV per atom and force less than 0.002 eV/Å per atom. The Perdew-Burke-Ernzerhof functional (PBE) with the Grimme-D3 vdW correction (PBE-D3) was used for geometry optimization. The elastic constants of violet phosphorous were calculated based on the energy-strain approach under the
approximation of Hooke’s law. The energy difference between the structure with \( E[V(\varepsilon_i)] \) and without stain \( (E[V(0)]) \) can be expressed as:

\[
\Delta E[(V(\varepsilon_i))] = E[V(\varepsilon_i)] - E[V(0)] = \frac{1}{2} V(0) \sum_{i,j=1}^{6} c_{ij} \varepsilon_i \varepsilon_j \tag{2}
\]

where \( c_{ij} \) and \( \varepsilon_i \) (\( \varepsilon_j \)) are the stiffness constants and strain, respectively.

For each distorted structure, we have applied strains \( \pm0.333, \pm0.667 \) and \( \pm1.000\% \), respectively.

The calculated stiffness tensor \( c_{ij} \) (GPa) with Voigt notation is

\[
\begin{bmatrix}
61.51 & 27.86 & 4.06 & 0.00 & -0.71 & 0.00 \\
27.86 & 50.89 & 1.63 & 0.00 & -5.74 & 0.00 \\
4.06 & 1.63 & 25.57 & 0.00 & -0.94 & 0.00 \\
0.00 & 0.00 & 0.00 & 7.79 & 0.00 & -5.27 \\
-0.71 & -5.74 & -0.94 & 0.00 & 11.14 & 0.00 \\
0.00 & 0.00 & 0.00 & -5.27 & 0.00 & 39.98
\end{bmatrix}
\]

(3)

9. The force curves of different layer violet phosphorene nanoflakes

![Force curves of different layer violet phosphorene nanoflakes](image)
Fig. S4 Fitting analyses of the force curves of different violet phosphorene nanoflakes. (a)10 layers, (b)12 layers, (c)13 layers, (d)16 layers, (e)18 layers, (f)25 layers, (g)36 layers and (h) 45 layers.

References